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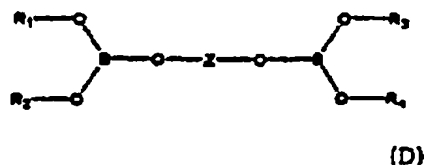
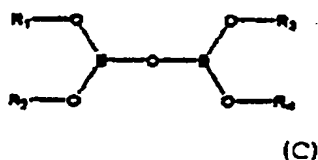
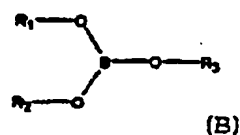
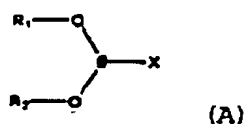
Esters as solvents in electrolyte systems  
for Li-ion storage cells

The invention relates to the use of specific esters of boric acid, carbonic acid, silicic acid, phosphoric acid and sulfuric acid as a solvent in electrolyte systems for Li-ion storage cells, to a composition comprising them and to Li-ion storage cells which contain these esters.

Until now, the solvents predominantly used in Li storage cells are alkyl ethers such as dimethyl ether, and alkene carbonates such as ethylene carbonate (EC) and propylene carbonate (PC). Such systems are described, inter alia, in JP 08 273 700 and JP 09 115 548.

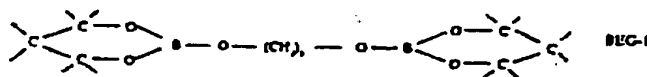
Also known, in addition, are electrolyte solutions based on various esters.

Thus, WO97/16862 describes an electrolyte solution which comprises boric acid esters of the following formulae (A) to (D):



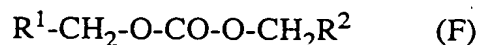
where X is halogen,  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  are straight-chain or branched-chain aliphatic or aromatic alkyls which may be substituted by substituents of various electronegativities and Z is a straight-chain or branched-chain aliphatic or aromatic alkyl or siloxane group.

An electrolyte solvent for rechargeable lithium and lithium-ion batteries based on a boric acid ester referred to as BEG-1, of the following formula (E), in combination with EC and/or PC is described in J. Electrochem. Soc., 143, p. 4047-4053, 1996.



(E)

EP-B 0 599 534 describes carbonate compounds of the following formula (F)



where  $R^1$  is a hydrogen, an alkyl or an alkyl substituted by one or more halogen atoms, and  $R^2$  is an alkyl which does not contain any  $\alpha$ -position

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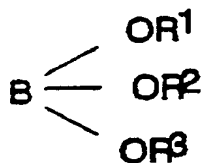
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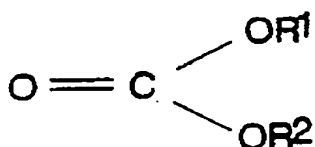
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For example, such electrolyte systems are to exist in the liquid phase over a relatively large temperature range while maintaining a low vapor pressure. They are to have a low viscosity in order thus to ensure sufficiently high conductivity. Moreover they are to be electrochemically and chemically stable and be sufficiently resistant to hydrolysis. In addition, such solvents should be capable of strong solvation of the ions of the conducting salts.

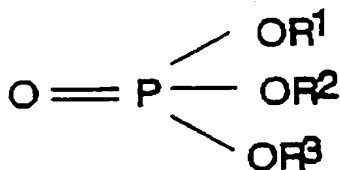
In view of the above prior art, it was an object of the present invention to provide novel solvents for electrolyte systems for Li-ion storage cells, which meet the increasing demands made of these solvents. The present invention therefore relates to the use of at least one ester of the formula (I) to (V)



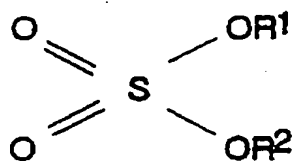
(I)



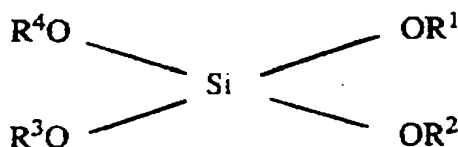
(II)



(III)



(IV)



(V)

where  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$ ,  $\text{R}^4$  are identical or different and each, independently of one another, are a linear or branched-chain  $\text{C}_1$ - to  $\text{C}_4$ -alkyl,  $(-\text{CH}_2-\text{CH}_2-\text{O})_n-\text{CH}_3$  with  $n=1$  to 3, a  $\text{C}_3$ - to  $\text{C}_6$ -cycloalkyl, an aromatic hydrocarbon group which in turn can be substituted, with the proviso that at least one of the groups  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$  or  $\text{R}^4$  is  $(-\text{CH}_2-\text{CH}_2-\text{O})_n-\text{CH}_3$  with  $n=1$  to 3, as a solvent in electrolyte systems for Li-ion storage cells.

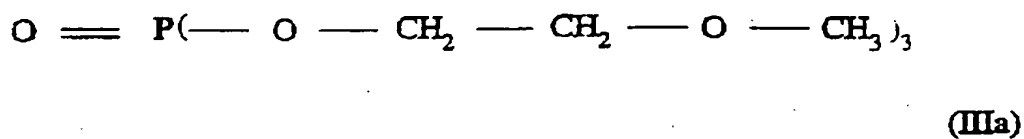
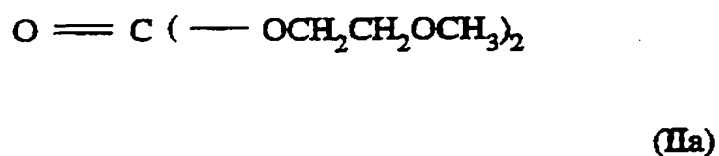
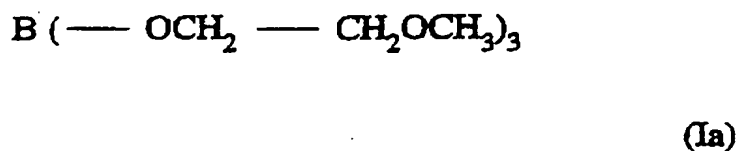
Among the abovementioned esters of formulae (I) to (V), the phosphoric acid esters of formula (III) are used preferentially.

Examples of the groups  $\text{R}^1$ ,  $\text{R}^2$  and, where present,  $\text{R}^3$  and/or  $\text{R}^4$  are methyl, ethyl, n- and isopropyl, n- and t-butyl, cyclopentyl, cyclohexyl and benzyl, and also  $(\text{CH}_2-\text{CH}_2-\text{O})_n-\text{CH}_3$  where  $n = 1$  to 3, although it should be noted, as previously mentioned, that at least one of the groups  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$  or  $\text{R}^4$  is  $(\text{CH}_2-\text{CH}_2-\text{O})_n-\text{CH}_3$  with  $n = 1$  to 3, preferably 1 or 2.

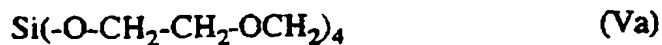
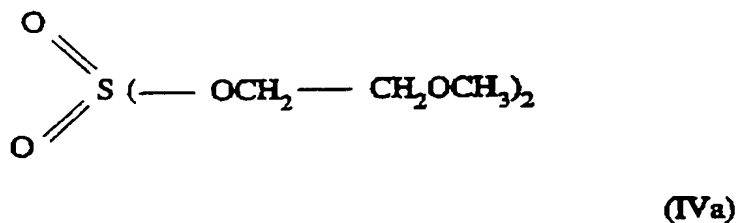
Greater preference is given to the use of esters of the formulae (I) to (V) in which  $\text{R}^1$ ,  $\text{R}^2$  and, where present,  $\text{R}^3$  and/or  $\text{R}^4$  are identical and are -

$\text{CH}_2\text{-CH}_2\text{O-CH}_3$  or  $(\text{-CH}_2\text{-CH}_2\text{-O})_2\text{-CH}_3$ , preference again being given to the corresponding phosphoric acid esters.

Examples of especially preferred compounds are the compounds of formulae  
5 (Ia) to (Va):



and



The esters used herein are eminently suitable, in terms of their properties, as solvents in electrolyte systems for Li-ion storage cells and generally have a viscosity, at room temperature, of  $\leq 10$  mPas, preferably  $\leq 5$  mPas and in particular  $\leq 3$  mPas. They have boiling points of, in general, about 200°C or more, preferably about 250°C or more and in particular about 300°C or more, in each case measured at atmospheric pressure, and have a sufficiently low vapor pressure, from roughly about  $10^{-5}$  to about  $10^0$  mbar at the temperatures of about -50°C to about 150°C encountered in the course of their use, so that they do not have an adverse effect on the characteristics of the Li-ion storage cell. Their boiling points mean that they are distillable and can therefore, in the course of their preparation, be obtained with high purity. Moreover, these esters, of a wide temperature range, are liquid at atmospheric pressure, generally still being liquid over a range extending as far as about -30°C, preferably as far as about -40°C. The esters described in this context can be employed as a solvent in electrolyte systems for Li-ion storage cells at at least about 80°C, preferably at at least about 120°C, more preferably at at least about 150°C.

Obviously, the esters used according to the invention can also be employed as a mixture with known solvents for electrolyte systems, e.g. the alkyl ethers mentioned at the outset, such as dimethyl ether, diethyl ether, dioxalane, diglyme, tetraglyme, 1,2-dimethoxyethane, tetrahydrofuran, 2-methyltetrahydrofuran, etc., and alkylene carbonates such as ethylene carbonate, propylene carbonate, butylene carbonate,  $\gamma$ -butyrolactone, and linear esters such as diethyl carbonate, dimethyl carbonate etc. Again, it is possible to employ a combination of at least one of the esters used according to the invention and at least one further solvent known from the prior art.

Preference is given to solvent combinations which have sufficiently low viscosity, are capable of strong solvation of the ions of the conducting salts, are liquid over a wide temperature range and are adequately electrochemically and chemically stable and resistant to hydrolysis.

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Furthermore, the esters employed according to the invention can also be employed in combination with polymer electrolytes, such as polymerization products, of boric acid esters, carbonic acid esters, silicic acid esters, phosphoric acid esters and sulfuric acid esters, whose constitution as a rule is such that at least one of the ester groups comprises a polymerizable unit such as a C=C double bond, and/or esters of the corresponding polyacids, for example polyphosphoric acid esters or polysilicic acid esters, and/or other conventional polymer electrolytes, the content of the esters used according to the invention being from about 5 to 100 wt%, preferably from about 20 wt% to 100 wt% and more preferably from about 60 wt% to 100 wt%, the total from ester and polymer electrolyte in each case adding up to 100 wt%.

The esters used according to the invention were prepared according to conventional methods, as described, for example, in K. Mura Kami in Chem. High Polymers (Japan), 7, p. 188-193 (1950) and in H. Steinberg, Organoboron Chemistry, Chapter 5, J. Wiley & Sons, N.Y. 1964. This generally involves starting from the acids, acid anhydrides or chlorides on which the esters are based, e.g. from boric acid,  $\text{C(O)Cl}_2$ ,  $\text{POCl}_3$ ,  $\text{SO}_2\text{Cl}_2$  and  $\text{SiCl}_4$ , these being reacted in a known manner with the corresponding mono- or polyhydric alcohols or etherols.

Exemplarily with regard to the preparation of a phosphoric acid ester, example 1a of the present invention describes a process in which trialkyl amine, which can be recycled subsequent to synthesis, is used as HCl scavenger.



In this process, the phosphoric ester of higher purity can be produced.

This concept can be transferred to the preparation of the other esters, as defined herein.

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Therefore, the present invention relates to a process of preparing an ester of formula (I) to (V), as defined above, characterized in that a chloride is employed as a starting material and a trialkyl amine is used as a scavenger for HCl formed during the preparation of the ester.

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In principle, each suitable trialkyl amine can be employed. Preferably, trimethyl amine, triethyl amine, tripropyl amine or a mixture of two or more thereof is employed, and, especially preferably, triethyl amine is employed.

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Preferably, the scavenger can be easily separated from the product, i.e. the ester. In a preferred embodiment of the present invention, the scavenger is separated from the product in a separatory funnel and then regenerated in a distillation.

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The esters employed according to the invention can be combined in conjunction with any of the conducting salts, as described, for example in EP-A 0 096 629, used hitherto for Li-ion storage cells. The use according to the invention preferably involves the use, as conducting salt, of  $\text{LiPF}_6$ ,  $\text{LiBF}_4$ ,  $\text{LiClO}_4$ ,  $\text{LiAsF}_6$ ,  $\text{LiCF}_3\text{SO}_3$ ,  $\text{LiC}(\text{CF}_3\text{SO}_2)_3$ ,  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ ,  $\text{LiN}(\text{CF}_3\text{CF}_2\text{SO}_2)_2$ ,  $\text{LiN}(\text{SO}_2\text{F})_2$ ,  $\text{LiAlCl}_4$ ,  $\text{LiSiF}_6$ ,  $\text{LiSbF}_6$  or a mixture of two or more thereof, the conducting salt used preferentially being  $\text{LiBF}_4$ . Particular preference is given to the use of the combination of the esters of formulae (Ia) to (IVa) in conjunction with  $\text{LiBF}_4$  as conducting salt, particular preference again being given to the combination of the ester of

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09555759.033000

formula (IIIa) with  $\text{LiBF}_4$  as conducting salt.

The invention therefore also relates to an Li storage cell which comprises at least one ester as defined above.

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Furthermore, the present invention relates to a composition comprising:

(A) at least one compound of formula (I) to (V) as defined above, and

10 (B) a conducting salt selected among:

$\text{LiPF}_6$ ,  $\text{LiBF}_4$ ,  $\text{LiClO}_4$ ,  $\text{LiAsF}_6$ ,  $\text{LiCF}_3\text{SO}_3$ ,  $\text{LiC}(\text{CF}_3\text{SO}_2)_3$ ,  
 $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ ,  $\text{LiN}(\text{SO}_2\text{F})_2$ ,  $\text{LiN}(\text{CF}_3\text{CF}_2\text{SO}_2)_2$ ,  $\text{LiAlCl}_4$ ,  $\text{LiSiF}_6$ ,  
 $\text{LiSbF}_6$  and a mixture of two or more thereof,

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*BB*  
*Ca* this composition preferably comprising, as the compound (A), at least one ester of formulae (Ia) to (Va), more preferably the ester of formula (IIIa), in each case in conjunction with  $\text{LiBF}_6$  and/or  $\text{LiBF}_4$  as compound (B).

20 In particular, the present invention relates to compositions comprising as

- component (B)  $\text{LiBF}_4$  or a mixture of  $\text{LiBF}_4$  and  $\text{LiPF}_6$  with a preferred molar ratio  $\text{LiBF}_4:\text{LiPF}_6$  of from 0.1:9.9 to 9.9:0.1 and as
- component (A) a mixture of one of the esters of formula (I) to (V), preferably the esters of formula (III) and especially the esters of the

25 formula (IIIa), and, if necessary, at least one further suitable solvent of the group comprising alkyl ethers as e.g. dimethyl ether, diethyl ether, dioxalane, diglyme, tetraglyme, 1,2-dimethoxyethane, tetrahydrofuran, 2-methyltetrahydrofuran and alkylene carbonates as, e.g., ethylene carbonate, propylene carbonate, butylene carbonate,  $\gamma$ -

30 butyrolactone and linear esters as, e.g., diethyl carbonate, dimethyl

carbonate, the ester hereby constituting 10 to 100 % by wt. of the mixture.

The present invention also relates to compositions comprising as

- 5 - component (B)  $\text{LiPF}_6$  and as
- component (A) a mixture of the ester of formula (IIIa) and at least one further suitable solvent of the group comprising alkyl ethers as, e.g., dimethyl ether, diethyl ether, dioxalane, diglyme, tetraglyme, 1,2-dimethoxyethane, tetrahydrofuran, 2-methyltetrahydrofuran and alkylene carbonates as, e.g., ethylene carbonate, propylene carbonate, butylene carbonate,  $\gamma$ -butyrolactone and linear esters as, e.g., diethyl carbonate, dimethyl carbonate, the ester of formula (IIIa) hereby constituting x %  
10 by wt. of the mixture, where  $10 \leq x < 100$ .

- 15 The solution of compound (B) in compound (A) is generally from about 0.2 to about 3 molar, preferably from about 0.5 to about 2 molar, more preferably from about 0.7 to about 1.5 molar.

Furthermore, the present invention relates to the use of the above-defined  
20 composition as an electrolyte system in Li-ion storage cells and to an Li-ion storage cell comprising a composition as defined above.

Within the scope of the novel Li-ion storage cell it is possible to use any of the cathode materials customary for Li-ion storage cells, such as  $\text{LiCoO}_2$ ,  
25  $\text{LiNiO}_2$ ,  $\text{Li}_x\text{MnO}_2$  ( $0 < x \leq 1$ ),  $\text{Li}_x\text{Mn}_2\text{O}_4$ , ( $0 < x \leq 2$ ),  $\text{Li}_x\text{MoO}_2$  ( $0 < x \leq 2$ ),  $\text{Li}_x\text{MnO}_3$  ( $0 < x \leq 1$ ),  $\text{Li}_x\text{MnO}_2$  ( $0 < x \leq 2$ ),  $\text{Li}_x\text{Mn}_2\text{O}_4$  ( $0 < x \leq 2$ ),  $\text{Li}_x\text{V}_2\text{O}_4$  ( $0 < x \leq 2.5$ ),  $\text{Li}_x\text{V}_2\text{O}_3$  ( $0 < x \leq 3.5$ ),  $\text{Li}_x\text{VO}_2$  ( $0 < x \leq 1$ ),  $\text{Li}_x\text{WO}_2$  ( $0 < x \leq 1$ ),  $\text{Li}_x\text{WO}_3$  ( $0 < x \leq 1$ ),  $\text{Li}_x\text{TiO}_2$  ( $0 < x \leq 1$ ),  $\text{Li}_x\text{Ti}_2\text{O}_4$  ( $0 < x \leq 2$ ),  $\text{Li}_x\text{RuO}_2$  ( $0 < x \leq 1$ ),  $\text{Li}_x\text{Fe}_2\text{O}_3$  ( $0 < x \leq 2$ ),  $\text{Li}_x\text{Fe}_3\text{O}_4$  ( $0 < x \leq 2$ ),  $\text{Li}_x\text{Cr}_2\text{O}_3$   
30 ( $0 < x \leq 3$ ),  $\text{Li}_x\text{Cr}_3\text{O}_4$  ( $0 < x \leq 3.8$ ),  $\text{Li}_x\text{V}_3\text{S}_5$  ( $0 < x \leq 1.8$ ),  $\text{Li}_x\text{Ta}_2\text{S}_2$

( $0 < x \leq 1$ ),  $\text{Li}_x\text{FeS}$  ( $0 < x \leq 1$ ),  $\text{Li}_x\text{FeS}_2$  ( $0 < x \leq 1$ ),  $\text{Li}_x\text{NbS}_2$  ( $0 < x \leq 2.4$ ),  
 $\text{Li}_x\text{MoS}_2$  ( $0 < x \leq 3$ ),  $\text{Li}_x\text{TiS}_2$  ( $0 < x \leq 2$ ),  $\text{Li}_x\text{ZrS}_2$  ( $0 < x \leq 2$ ),  $\text{Li}_x\text{NbSe}_2$   
( $0 < x \leq 3$ ),  $\text{Li}_x\text{VSe}_2$  ( $0 < x \leq 1$ ),  $\text{Li}_x\text{NiPS}_2$  ( $0 < x \leq 1.5$ ),  $\text{Li}_x\text{FePS}_2$   
( $0 < x \leq 1.5$ ) and a mixture of two or more of these, possibly together with  
5 a binder such as polytetrafluoroethylene and poly(vinylidene fluoride).

The anode material used may likewise be any of the anode materials customarily employed in Li-ion storage cells, such as metals, for example metallic lithium, lithium-containing metal alloys, a metal sulfide or a carbon-  
10 containing material, especial preference being given to carbon-containing materials which are capable of storing and releasing lithium ions. To be mentioned among carbon-containing materials of this type are natural and synthetic graphite or amorphous carbon such as activated carbon, carbon fibers, synthetically graphitized coal dust and carbon black. It is also  
15 possible to use oxides such as titanium oxide, zinc oxide, tin oxide, molybdenum oxide, tungsten oxide, and carbonates such as titanium carbonate, molybdenum carbonate and zinc carbonate.

Further details regarding suitable anode and cathode materials and the  
20 fabrication of the Li-ion storage cells can be gathered from the prior art mentioned at the outset, which is incorporated by reference.

If required, the solvent according to the invention may also be admixed with solids such as  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ .

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The fabrication of the Li-ion storage cells generally involves the coating of the current collector electrodes with the anode or cathode material, the insertion of spacers e.g. made of stretched polypropylene, and the addition of the electrolyte, after which this system consisting of cathode, anode,  
30 spacer and electrolyte is wrapped and inserted into a jacket.

The present invention will now be explained in more detail with reference to a few examples according to the invention and with the aid of Figures

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5 where Figure 1 depicts a cyclovoltammogramm (CV) in the voltage window from 0 to 4.3 V, recorded with the test cell according to Example 2,

Figure 2 depicts a CV in the voltage window of a lithium-ion battery from 3.3 to 4.3 volts, recorded with the test cell according to Example 3,

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Figure 3 depicts a CV in the voltage window of from 2.75 to 4.5 volts, recorded with the test cell according to Example 4.

#### EXAMPLE 1

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To prepare the phosphoric ester of formula  $\text{O}=\text{P}(-\text{O}-\text{CH}_2-\text{CH}_2-\text{OCH}_3)_3$ , 274 g (3.6 mol) of methylglycol together with 2 g of  $\text{ZnCl}_2$  were introduced as the initial charge into a 1,000 ml round-bottomed flask and cooled to 5°C. Then, 153.33 g (1 mol) of  $\text{POCl}_3$  were added dropwise over  
20 a period of 50 min, the temperature being maintained at approximately 5°C to 10°C. After the addition was complete, a clear solution was obtained which was allowed to warm to room temperature. The product mixture obtained was then distilled in vacuo (80 to 90 mbar) at about 50°C to 55°C, to remove unreacted starting material and by-products.

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Distillation then continued in high vacuum (about 0.02 mbar) at about 170°C, affording the desired product. The water content of the above phosphoric ester was 20 ppm.

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### EXAMPLE 1a

To prepare the phosphoric acid ester of the formula  $O=P(-O-CH_2-CH_2-O-CH_3)_3$ , 137 g (1.8 mole) methylglycol and 1 g  $ZnCl_2$  were introduced as  
5 initial charge into a flask. In a nitrogen atmosphere, 570.75 g toluene were added while the mixture was stirred. Then, 151.8 g triethyl amine were added dropwise and the content of the flask was cooled to 5°C. Then, 76.7 g  $POCl_3$  were added dropwise within 30 min, the temperature being maintained at approximately 5 - 10 °C. After the addition was complete,  
10 cooling was turned off. While stirring the temperature of the solution rose to 23 °C.

Then, the solution was heated to 110 °C, refluxed within approximately 1  
15 to 1.5 h and cooled to room temperature.

While the solution was stirred vigorously, 360 g of the 20 % by wt. NaOH solution was added dropwise and the resulting solution transferred to a separatory funnel in which the phases were separated.

20 From the lower, aqueous phase the triethyl amine was regenerated by means of distillation.

From the upper, organic phase the toluene was removed under standard pressure by means of distillation. Afterwards, under high vacuum at a  
25 pressure of 0.3 mbar and at a temperature of approximately 170 °C, the product, the phosphoric acid triester, was separated by means of distillation.

Compared to example 1, example 1a provides a product having a lower water content (15 ppm). A further advantage of example 1a is an enhanced  
30 purity of the product, i.e. the amount of phosphoric acid triester could be

increased compared to, e.g., phosphoric acid diester.

## EXAMPLE 2

5 The product of composition  $\text{O}=\text{P}(-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_3)_3$  and a highly pure conducting salt  $\text{LiPF}_6$  were used in the preparation, under an inert-gas atmosphere, of a 0.1 M electrolyte. This electrolyte was then used in the assembly of a 3-electrode cell comprising platinum as the working electrode, platinum as the counterelectrode and a Li metal strip as the reference  
10 electrode for electrochemical measurements.

This electrochemical test cell was then used to record a cyclovoltammogramm in the voltage window from 0 to 4.3 volts versus  $\text{Li}/\text{Li}^+$ , to determine the electrochemical stability of this solvent.

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The measuring conditions were as follows:

Starting from the open-circuit potential, oxidation was first carried out as far as 4.3 V, at a constant scan rate of 0.1 mV/sec, followed by reduction as far as 3.0 V. Subsequently, a further cycle was run in this voltage window.

20 Figure 1 shows that the abovementioned phosphoric acid ester is electrochemically inert in the voltage range customarily used in rechargeable lithium-ion batteries and is therefore suitable as an electrolyte solvent.

## EXAMPLE 3

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By a method similar to that of Example 2, an electrochemical 3-electrode test cell was again assembled, except that this time a 0.5 M  $\text{LiPF}_6/\text{O}=\text{P}(-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_3)_3$  electrolyte was used. The working electrode used in this case was an Li-manganese spinel coating on aluminum foil, and Li metal  
30 was used as the counter and the reference electrode.

In the typical voltage window of a lithium-ion battery, from 3.3 to 4.3 volts, a cyclovoltammogram was again run at a scan rate of 0.01 mV/sec, which is realistic for batteries.

- 5 As can be seen from Figure 2, the twin redox peak, typical for such a spinel, was produced both in the course of oxidation (= extracalation of the Li ions from the spinel host lattice) and of reduction (= intercalation of Li ions into the spinel host lattice). The electrolyte used can therefore be employed for rechargeable lithium-ion batteries comprising Li-manganese spinel cations.
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#### EXAMPLE 4

- The product of composition  $\text{O}=\text{P}(-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_3)_3$  and a highly pure conducting salt  $\text{LiBF}_4$  having a concentration of 1 M in the ester  $\text{O}=\text{P}(-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_3)_3$  were used in the preparation, under an inert-gas atmosphere, of a 0.1 M electrolyte.
- 15

Measuring conditions:

- 20 Starting from the open-circuit potential, oxidation was first carried out as far as 4.3 V vs.  $\text{Li}/\text{Li}^+$ , at a scan rate of 0.33 mV/sec, followed by reduction as far as 3.3 V. Subsequently, 2 full cycles were run in this voltage window.

- As Figure 3 shows, this electrolyte too is stable in the voltage window of the lithium-ion battery and can thus be used as an electrolyte system.
- 25